



Full Length Article

Enhancement of activity and hydrothermal stability of Pd/ZrO₂-Al₂O₃ doped by Mg for methane combustion under lean conditions



Wei Hu^a, Guangxia Li^a, Jianjun Chen^b, Fujin Huang^a, Maochu Gong^b, Lin Zhong^{a,*}, Yaoqiang Chen^{b,*}

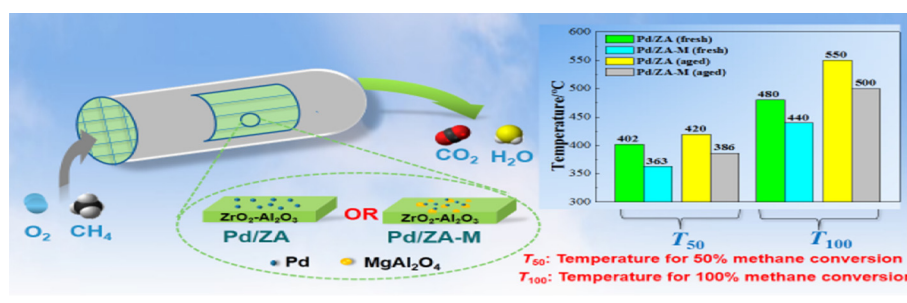
^a College of Chemical Engineering, Sichuan University, Chengdu 610065, PR China

^b Key Laboratory of Green Chemistry and Technology of the Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, PR China

HIGHLIGHTS

- Pd supported on ZrO₂-Al₂O₃ composite doped by Mg was developed.
- The formed MgAl₂O₄ spinel stabilized Pd²⁺ species and inhibited the formation of hydroxyl groups.
- The Mg-doped catalyst displayed higher Pd dispersion.
- The doped catalyst showed significantly enhanced performance for methane oxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

By a facile doping strategy, a new Pd catalyst supported on ZrO₂-Al₂O₃ composite doped by Mg was developed. The catalyst was carefully characterized by X-ray diffraction (XRD), CO chemical adsorption, transmission electron microscope (TEM), NH₃ temperature programmed desorption (NH₃-TPD) and X-ray photoelectron spectroscopy (XPS). The results revealed that the physical and chemical properties of the catalyst can be modulated by Mg dopant. An MgAl₂O₄ spinel was formed by Mg doping, which can stabilize Pd²⁺ species and inhibit the formation of hydroxyl groups on the surface of support. Compared with its analogous catalyst without Mg dopant, the Mg-doped catalyst had higher Pd dispersion and smaller Pd nanoparticles. Moreover, a more suitable acidity for methane oxidation can be generated on the surface of the catalyst upon Mg doping. Therefore, the introduction of Mg doping strongly enhanced the low-temperature activity and hydrothermal resistance of the catalyst for the total oxidation of methane under lean conditions. Notably, the complete conversion temperature of methane can be decreased significantly by 40–50 °C with the doped catalyst before and after harsh hydrothermal aging treatment.

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1. Introduction

Over the past two decades, lean-burn natural gas vehicles (NGVs) have been attracted extensive attention due to its high fuel-efficiency and less pollution [1]. However, the unburned methane from NGVs emissions is causing big problems because

of its significant greenhouse effect [2]. Removal of unburned methane by catalytic oxidation has been proved the most effective method to address the problems, and Pd catalysts on Al₂O₃-based support have shown the highest catalytic activity for the oxidation [3,4]. Generally, in the literature, the active phase for methane oxidation of Pd-based catalysts is PdO [5]. Nonetheless, these catalysts normally suffer from poor low-temperature activity and rapid deactivation under the real reaction conditions such as temperature of 500–550 °C and steam of 10–15% (v/v). Currently, complete oxidation of the unburned methane at temperatures below 500 °C

* Corresponding authors.

E-mail addresses: zhonglin@scu.edu.cn (L. Zhong), nic7501@scu.edu.cn (Y. Chen).

in the presence of 10–15 vol% H₂O is still very challenging. Developing new Pd catalysts with enhanced performance is thus highly desired [3,6].

Recently, Pd catalyst supported on ZrO₂-Al₂O₃ composite, Pd/ZrO₂-Al₂O₃, shows improved activity and stability compared with Pd/Al₂O₃ in the methane removal for NGVs [7–11]. The enhancement may be due to that the interaction between Pd and Zr inhibits the aggregation of Pd and improves the redox properties of Pd⁰/Pd²⁺ [7], and that the abundant oxygen vacancy on ZrO₂-Al₂O₃ support can promote the methane oxidation greatly [8,9]. Furthermore, high Pd dispersion on the catalysts because of the strong interaction between Al₂O₃ and ZrO₂ also enhances the low-temperature activity significantly [10,11]. However, there is still room to further improve the activity and hydrothermal stability of these catalysts to meet the more rigorous emission regulation [12–14].

Very recently, a doping strategy by which dopant tailors the physical and chemical properties of host catalyst and modifies favourably its activity and stability has been successfully developed for catalysis, especially for oxidation catalysis [15–21]. However, to the best of our knowledge, no work to modify Pd/ZrO₂-Al₂O₃ by doping strategy for methane oxidation has been reported. Herein, a new Mg-doped Pd/ZrO₂-Al₂O₃ catalyst with enhanced activity and hydrothermal stability was developed by a facile doping strategy for methane oxidation under lean-burn conditions [22–24].

2. Experimental

2.1. Support preparation

The Zr_{0.5}Al_{0.5}O_{1.75} support, marked as ZA, was obtained by co-precipitation method as described elsewhere [11]. Briefly, the desired mixture aqueous solution of ZrO(NO₃)₂ and Al(NO₃)₃·9H₂O (molar ratio 1:1) was precipitated by ammonia at pH ≈ 10. After co-precipitation process, the prepared precipitates were filtered, washed, dried and then calcined at 600 °C for 3 h. Mg-doped ZA support was prepared by an impregnation method using Mg(NO₃)₂·6H₂O aqueous solution and the Mg loading was 5 wt%. The obtained powder was dried at 120 °C for 12 h, and then calcined in air at 950 °C for 3 h. The corresponding supports were named as ZA-M.

2.2. Catalyst preparation

The as-synthesized ZA- and ZA-M-supported Pd catalysts (Pd/ZA and Pd/ZA-M) with 1.5 wt% Pd loading were prepared by incipient wetness impregnation method, and followed by drying at 120 °C for 12 h and calcining at 550 °C for 3 h. To evaluate the hydrothermal stability of the catalysts, Pd/ZA and Pd/ZA-M were treated at 750 °C for 10 h under air (1280 ml L⁻¹) flow with 10 vol% H₂O. The resulted aged catalysts were named as Pd/ZA (A) and Pd/ZA-M (A), respectively. The catalyst powders were ball milled with a binder (1.0 wt%, ZrO(Ac)₂) to form a slurry, and then coated on a commercial monolithic cordierite (400 cell per inch², Corning, America) containing monolith catalyst was ca. 150 g L⁻¹. The as-synthesized catalyst and monolithic catalyst was obtained by drying overnight at 120 °C and calcining for 3 h at 550 °C under airflow.

2.3. Catalyst characterization

Specific surface area, average pore size and total pore volume of the as-prepared catalysts were measured with N₂ adsorption-desorption experiments at 77 K (Autosorb SI, Quanachrome,

USA). Prior to analysis the catalysts were degassed in vacuum at 300 °C for 3 h. The specific surface area was calculated according to the BET method, and the total pore volume was analyzed using BJH method.

The crystal structures of catalysts were detected by X-ray powder diffraction (XRD), and the X-ray diffraction data were obtained by powder XRD on D/Max-rA using Cu K α radiation ($\lambda = 0.15406$ nm) that operated at 40 kV and 25 mA. The samples were scanned from 10° to 70° with an interval of 0.06°.

The metal Pd dispersions of the catalysts were calculated from CO chemisorption experiments by the pulse method at room temperature. The calcined samples (200 mg) were packed in a quartz U-tube reactor. Prior to CO chemisorption, the catalysts were heated from 25 to 500 °C at a rate of 10 °C min⁻¹ and reduced in a flow of H₂ (25 ml min⁻¹) at 500 °C for 1 h, and then cooled to room temperature in flowing Ar (25 ml min⁻¹). CO chemisorption experiments were performed by dosing 5% CO/He gas mixture at room temperature. The effluent gas was analyzed with an on-line gas chromatograph equipped with a thermal conductivity detector (TCD).

Transmission electron microscopy (TEM) was carried out on a Tecnai G2 F20 S-TWIN to characterize the morphology of catalysts. Typically, the catalysts powders were dispersed into ethanol, followed by treated with sonication for 0.5 h and by drop-casting of the dispersion onto holey carbon coated 300 mesh Cu grids.

For the acidity analysis of supports, NH₃-TPD analysis was carried out on a commercial instrument (Xianquan, TP5076) with a TCD detector at a linear heating rate of 10 °C min⁻¹ from 25 to 500 °C. 100 mg sample was pretreated under He flow (30 ml min⁻¹) at 500 °C for 1 h. After the pretreatment, the samples were cooled from 500 to 80 °C at a rate of 10 °C min⁻¹ and NH₃ was flowed over the supports for 60 min to ensure the maximum adsorption at 80 °C, and then pretreated under He flow at 80 °C for 3 h. The measurements were performed at a linear heating rate of 10 °C min⁻¹ from 80 to 800 °C under He (30 ml min⁻¹) flow.

H₂-temperature-programmed reduction experiments were performed using a quartz tubular micro-reactor equipped with a thermal conductivity detector. Before measurement, the samples (100 mg) were pre-cleaned in N₂ (30 ml min⁻¹) flow holding at 500 °C for 60 min, and then cooling to room temperature. The data was measured from room temperature to 900 °C in 5% H₂/N₂ (30 ml min⁻¹) at a heating rate of 10 °C min⁻¹.

The X-ray photoelectron spectroscopic (XPS) data were determined by an electron spectrometer (XSAM-800, KRATOS Co.) equipped with an Al K α radiation as a primary excitation. Binding energies were calculated on the basis of C 1s at 284.6 eV.

2.4. Catalytic activity tests

Activity measurements for methane oxidation were carried out in a fixed-bed quartz flow reactor at atmospheric pressure and the schematic of the system is shown in Fig. 1. The temperature was measured by a K-type thermocouple placed at the front face-center of the monolith catalyst. The other K-type thermocouple connected with a temperature controller instrument was used to monitor the temperature at the outer edge of the specific place of the reactor where the monolith catalyst was placed. The simulated NGVs exhaust gases was controlled by mass flow controllers and consisted of 750 ppm CH₄, 0.1 vol% CO, 5.0 vol% O₂, 12.0 vol% CO₂, 12 vol% H₂O and N₂ as balance gas. The experiment was carried out at a gas hourly space velocity of 50,000 h⁻¹. The gas composition at outlet was continuously analyzed by an FT-IR (Antaris IGS, Thermo Fisher Scientific). The methane conversion was calculated by following equation:

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